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Procedia Engineering 44 (2012) 649 – 652

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[OD54]
Asymmetric track-etch pores for micro- and nanofluidics

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Narrow pores produced by the track-etching process in dielectric foils have been successfully used as model cylindrical channels with electrically charged walls since the 1970-s [1, 2]. The behavior of ion flow in electric field that is confined in a relatively narrow space has become a subject of numerous experimental and theoretical studies during the last decade. The rapidly growing interest in artificial nanopores is induced by biological and nanotechnological aspects [3, 4]. Conical ion track nanopores have been developed to approach the geometric characteristics of the ion channels in living matter [5]. It has been demonstrated that the conical nanopores in polymers such as polyethylene terephthalate (PET) and polyimide are cation selective and possess diode-like current-voltage characteristics. Several intriguing phenomena have been found for asymmetrical nanopores: ion current rectification, ion enrichment, ion depletion and “nanoprecipitation” induced by a voltage applied to the pore. Many of the properties of the asymmetrical pore are determined by its geometry. In the present report, different track-etching procedures that allow fabrication of asymmetric nanopores with pre-determined geometry are presented.

Polyethylene terephthalate films of different thickness (5, 12 and 23 μm) were irradiated with accelerated heavy ions to produce straight-through tracks in the foils. The ion fluence ranged from 10^4 to 10^8 cm^{-2}. Samples with single tracks were also studied. Special etching techniques were applied to produce asymmetric pores in the ion-irradiated PET foils. Alkaline solution (either surfactant-doped and surfactant-free) were used to develop the asymmetric pores of various geometries [6, 7]. The etched samples were examined using a field emission scanning electron microscope. Pore profiles were determined via imaging of fractures of membranes obtained. Current-voltage characteristics of the samples were determined using an electrolytic cell with Ag/AgCl electrodes, filled with KCL solutions of various concentrations. The transmembrane current I was measured by stepping the voltage between +1 and –1 V.

One-sided etching with electro-stopping provides conical nanopores. Asymmetric etching using a surfactant-doped etchant opens up a possibility of creating longitudinal profiles other than conical, i.e. with degree of taper that varies along the pore. One-sided pre-treatment with ultra-violet radiation and subsequent two-sided etching in the surfactant-doped alkaline solution makes it possible to fabricate pores with a highly-tapered (“bullet-like”) pore tip. Formation of nanopores with different tip shapes is based on the interplay between chemical attack by alkali and protection effect of surfactant. These two components of etching solution diffuse into the pore at different rates. Varying the etchant component concentrations makes it possible to tune the degree of taper and, thus, the ion current rectification properties of the nanopore. Examples of pore geometries are shown in Figure 1.

In electrolyte solutions, the asymmetric pores with a highly-tapered tip exhibit substantially non-linear current-voltage characteristics (see Figure 2). The rectification effect, defined as the rectification ratio $r = I(-1\text{ V}) / I(+1\text{ V})$, was calculated from the measured I-V-characteristics for each KCl concentration. The behavior of the rectification ratio depending on electrolyte concentration is shown in Figure 3. The data for four samples with gradually increasing tip diameters are presented. The rectification ratio peaks at KCl concentrations 0.05-0.1 M. Similar behavior was predicted theoretically and observed earlier for conical pores [8]. However, the rectification ratios for the bullet-like pores are higher than those for conical ones. Calculations based on the Poisson and Nernst-Planck equations [9] confirm that the channels with highly-tapered tips should exhibit a strong asymmetry with regards to ion transport. The theoretical simulation shows that the position of the rectification maximum mainly depends on the surface

doi:10.1016/j.proeng.2012.08.518

charge density on pore walls. The curves measured experimentally correspond to the negative charge density of 0.3-0.5 e/nm^2.

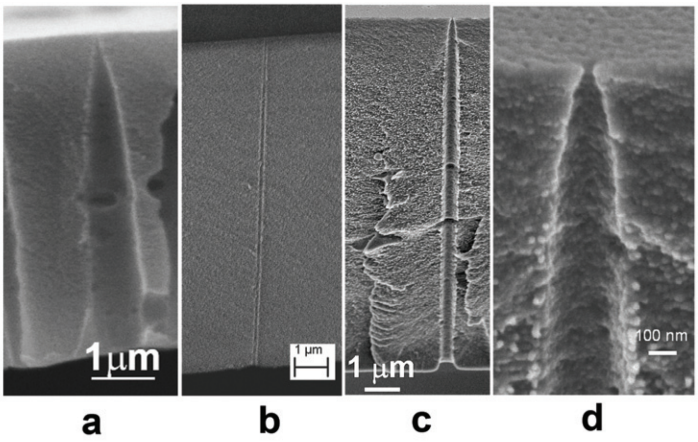

Figure 1. FESEM images of asymmetric pores in a 12 μm thick PET foil: (a) with a wide cone angle; (b) with a slightly-tapered tip; (c) with a highly-tapered tip (bullet-like); (d) the bullet-like tip at a higher magnification. All the pores have a small pore diameter of several tens of nanometres.

Among all of the structures fabricated and tested in this work, the asymmetric bullet-like pores with a tip radius of 13 to 20 nm and a base radius of 100 to 150 nm (see Figure 1c) showed the highest rectification. In contrast, the conical pores that widen too much (see Figure 1a) showed almost symmetric current-voltage characteristics. Therefore, we have found an optimum shape of pores to be used as nanofluidic diodes. In experiments with foils 5, 12 and 23 μm thick we have also observed that the rectification effect increases with increasing membrane thickness, i.e. with increasing pore length. The higher rectification observed for longer pores could be a result of a surplus of restricted volume in which ion enrichment and depletion take place at opposite voltage polarities.

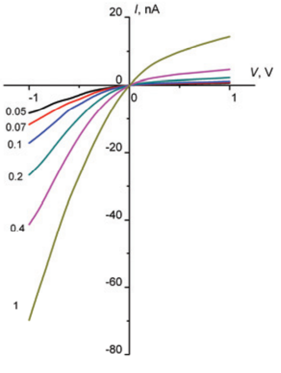

Figure 2. Current-voltage characteristics of a membrane with highly-tapered pore tips recorded in KCl solutions. The concentrations of KCl (in mol/L) are shown at the curves on the left. The current *I* is normalised to one pore. The state with high conductance is observed when positive voltage is applied to narrow end of the pore.

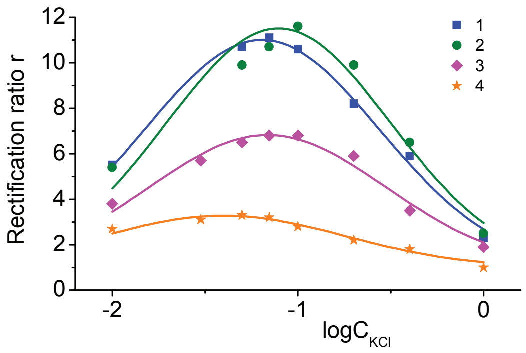

Figure 3. Rectification ratio vs. concentration of KCl for asymmetric membranes 12 μm thick, etched in surfactant-doped 6M NaOH to produce channels with bullet-like tips. Etching time is 2.5 min (1), 3.5 min (2), 5min (3) and 6.5 min (4). Sample 2 has a tip diameter of about 36 nm and shows the highest rectification effect.

The same ion track etching technique allows control over the hydraulic resistance of the membrane. The diameter of wide part of pores provides for a relatively high flow rate through the membrane whereas the small diameter of pore necks governs the retention properties. Our study shows that the degree of tapering and, thus, the viscous flow rate can be varied at will. A wide variety of pore configurations can be achieved and used as micro- and nanofluidic channels. This study paves the way for the design of membranes with specific functions. A simple chemical procedure of track etching allows one to tailor the viscous flow and ion transport properties of a nanopore system. Track-etched nanopores with bullet-like tips have short selective channels; therefore, such membranes can be regarded as analogues to nanopores in thin films. At the same time, the membranes are thick, robust, and easy to handle.

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Keywords: ion track, nanopore, electric conductance, ion current rectification